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death kindles our zeal to stop the spread of infection, to discover the means of preventing the suffering, and, when this is not possible, to surround the lonely sick and dying with the best medical skill, attention and kindness that is possible. The desolation of their appalling loneliness is often doubtless greater than that of their illness and oncoming death combined."

PHILADELPHIA, April 4, 1903.

## ON ARTIFICIAL PRODUCTION OF CRYSTALLIZED DOMEYKITE, ALGODONITE, ARGENTODO- MEYKITE AND STIBIODOMEYKITE.

(Plate V.)

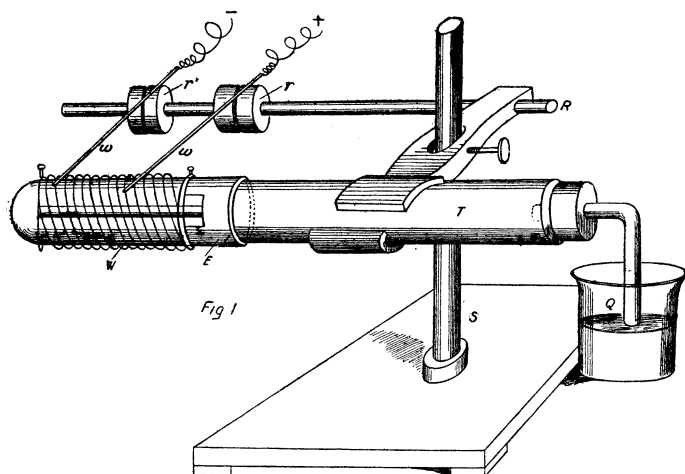
BY GEORGE A. KOENIG.

(Received June 1, 1903.)

In a paper on mohawkite, domeykite and other copper arsenides of the Mohawk mine (*Zeitsch. f. Krystall.*, etc., Vol. xxxiv, 1 Heft), I mentioned some attempts made by me to obtain domeykite in measurable crystals by the action of arsenic vapors upon metallic copper. One experiment gave crystals, although not measurable, but further trials failed at the time, evidently through my inability to maintain the proper temperature by means of an Erlenmeyer combustion furnace. The range between the temperature at which the crystals form and that at which the crystals melt is a very narrow one. On the other hand the eagerness with which the copper absorbs the arsenic causes heat, and hence the difficulty in adding just the right quantity of thermal energy from the outside. It occurred to me to try an electric current as a source of heat. The very first trial gave most promising results. The experiments were taken up in November, 1900, and continued until March, 1901. The adjoining figure illustrates the simple apparatus which proved itself adequate to all requirements.

In watching the rapid growth of the crystals the similarity of the phenomenon with the development of an egg occurred to me, and I applied the name "incubator" to the apparatus, than which no other could be more expressive.

The incubator consists of a piece of combustion tubing (T), closed at one end. The length is unimportant since only about three inches of it are in actual use. I have varied the diameter from three-eighths to three-fourths inch with no apparent difference in the action. The crystals do not grow any larger in a large tube than in a small one. Around the tube is wound a very thin platinum wire (W), beginning at the closed end. In order to keep the coils separated I laid three strips of thin asbestos paper (E) lengthwise upon the glass and then began winding. The first turn returns to the start, a twist is made, and thus a well-fixed start is secured



which will prevent the wire from slipping. The pitch of the thread will be governed by the maximum of heat desired. This will be variable with different metals and may be varied even for the same metal, as I have frequently done, the variation being between one-eighth and one-thirty-second of an inch. The last coil is secured in the same way as the first. Two inches of winding were mostly sufficient. Whenever the glass gets to full red heat the wire will fuse into it and will be broken in unwinding. To avoid this spoiling of the wire it would be the best thing to cover the whole glass surface with the asbestos sheet. But doing so would also prevent the observation of the phenomena occurring within. One might as well, or even preferably, use a porcelain tube. One would have to forego the great pleasure of seeing the so-called inanimate things

come to life, and one would make many more failures by either too much or too little heat. The wear and tear of the wire seems trifling when held against this loss. Being thus prepared the tube is ready to be charged.

At A (Fig. 2) I place from five to ten grams of resublimed arsenic, on top of this a loose plug of asbestos (P). In the first experiments I thought copper filings would be the best material to

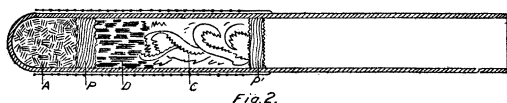


Fig. 2.

act upon. These filings I poured on top of P, forming a column about one inch high, and secured this column by means of a second asbestos plug (P'). Such an arrangement of parts promised to restrain the arsenic vapors from passing by the copper without action. It proved an unnecessary precaution, as the copper acts toward that vapor as a sponge toward water. Coarse turnings were tried instead of filings, and later solid copper bars with even better results than the filings had given. Similarly the close proximity of the copper to the plug P was found objectionable and, therefore, in all the later experiments the tube was placed, after charging the arsenic and inserting P, in a horizontal position by means of a clamp at the open end. Then the metal pieces to be acted upon were shoved into the desired distance from the plug, a loose asbestos plug next to the metal to avoid air currents, and finally a stopper holding a narrow glass tube, bent at right angles, was inserted into the open end. The glass tube was then made to dip under mercury and thus expansion of the air made possible, without danger of air entering. Whatever oxygen was in the tube made  $\text{As}_2\text{O}_3$ , which was always found as a ring sublimate behind the metal. Fig. 1 shows the outside of the tube, clamped to the stand S. The stout contact wires, w, w', were found very serviceable. By their use the field of high temperature may be enlarged or restricted as well as shifted. These wires are simply laid upon the coil wire. Their position must not be shifted or altered without switching off the current; the thin wire will melt in the moment when the contact is broken. I spoiled considerable wire in this way, besides the time consumed in rewinding is quite an item. A suitable, easily changeable resistance to modify the tone of the

thermic energy is made part of the circuit. A water resistance answers very well if a Mariotte's bottle be provided to keep the water level, and if the one wire be fastened to a swivel; the latter arrangement permits a quick and easy modification to  $\frac{1}{1000}$  amps. In my work with the incubator a drum resistance coil with roller contact was used. The apparatus was placed into a dark room in which the faintest glow could be seen and thus the lower limit of temperature was probably  $450^{\circ}$  C., with the upper limit of C.  $500^{\circ}$  to  $700^{\circ}$ . The most satisfactory range for domeykite is about  $600^{\circ}$  C.

#### AIMS OF THE INVESTIGATION.

At the start the aim was not so much the mere production of domeykite crystals, as the demonstration that nickel and cobalt might replace copper in the molecule without changing the symmetry, in other words to establish the isomorphous character of domeykite and mohawkite. This original scope became at once wider, when the results showed the ease with which domeykite was formed in good crystals. The action of arsenic upon iron, lead, silver, cobalt, nickel was included and equally satisfactory results were fondly hoped for.

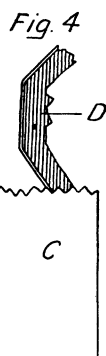
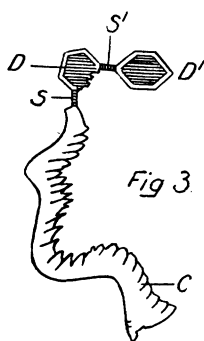
A still farther circle could be described by drawing in antimony since silver was known to unite with antimony as  $\text{Ag}_3\text{S}_6$ . The hopes were not realized. Under other conditions perhaps better results may be obtained, at least in some cases. I am referring here to the action in vacuo. Up to this time I have not tried the vacuum, so much other work is constantly crowding in. I will not pre-empt work in this line and shall gladly see any colleague step in to take up this undoubtedly highly interesting work.

#### I. ACTION OF ARSENIC VAPORS UPON COPPER IN THE INCUBATOR —DOMEYKITE.

*a.* Coarse copper turnings were placed in the tube (C. Fig. 2) so that about three-fourths inch of free space were left between the copper and the asbestos plug P, and the contact wires were so placed that the evaporation of the arsenic was fairly rapid, whilst the temperature of copper remained near the lower limit of say  $500^{\circ}$  C. Soon one saw shooting out from the copper very thin, brilliant leaves. The direction of growth was parallel with the tube's axis. The growth keeps up until the entire free space is filled with the bright crystal aggregate. The latter looks much like sublimed arsenic, and that I

thought it to be until the analysis showed it to contain 72.9 per cent. of copper. The crystals even penetrated into the asbestos, and from this very extremity the material for the analysis was taken. This experiment was carried on from 8 A.M., January 11, 1900, for forty hours. Here was a phenomenon of molecular or ionic activity without parallel; at least to me extraordinary, for I had not seen any record of a similar observation. It is not difficult to understand the building up of crystals from a medium which contains the molecules in the liquid or gaseous state. But what I observed here implied a very different condition of things. Not even the skyward growth of a tree, which somewhat resembles this stretching out of the domeykite toward the supply of arsenic, is comparable. For the cells draw their nourishment from the liquid sap and the gaseous air. The growing may happen from the root by pushing or by growing at the front. In the latter case the copper ions must be supposed to be going like the ions under the direction of a current, but going in the solid condition, and this is the point at which the imagination recoils. Either alternative rests upon a push or a draw impulse. The present experiment would seem to point toward a push from the root as the cause, that is to say to a mobility of the copper arsenide molecule  $\text{Cu}_3\text{As}$ . In Fig. 3 is represented one of the results of a later experiment, which gives support to the notion that the copper ions are moving and not the molecule  $\text{Cu}_3\text{As}$ . Here C is a piece of copper turning. On a slender stylus S sits the large domeykite crystal D (the tabular type, three millim. in diameter). The crystal is incomplete on one side. From it leads a second stylus  $\text{S}^1$ , and upon this another somewhat incomplete crystal of domeykite D has been growing. All the material for the crystals must have come through the stylus S. Instead of all the *material*, I should say more correctly all the copper. The stylus habit for the crystallization is very common; Fig. 3 merely represents an unusually fine specimen of this habit. Looking at the phenomenon of molecular mobility in the solid state merely as a physico-chemical process, aside from crystallization, I can see an analogous occurrence in the so-called cementation process of steel or case-hardening process. In this process a bar of soft iron is exposed to red heat in a packing of solid charcoal, and becomes gradually converted into carbide  $\text{Fe}_3\text{C}$  to the very innermost parts. It would seem that the solid carbon ions become mobilized, passing from one group of iron ions to the next until

chemical saturation has been reached. To my knowledge, however, no experiments have been put on record which absolutely precluded the coaction of gasified carbon as CO; I mean that the experiments were not carried on in perfectly air-tight vessels. Yet, granted even that the solid carbon travels by exchange through a bar of iron, the phenomenon is not quite correlated to our problem. For if the two were similar then the arsenic would have to penetrate to the core of the copper chip without altering practically its original shape. But in the specimen Fig. 3 the copper chip C is perfectly bright metallic copper, even immediately under the stylus S. Furthermore all the other metals behaved toward arsenic vapors as iron toward carbon: the arsenic penetrates



and crystals do not shoot forth. Copper possesses, therefore, a *unique ionic mobility*. Since copper stands at the head as a conductor of both heat and electricity, may not this be due to that mobility of the ions?

b. If a copper chip be placed into the incubator and both resistance and contact wires be so adjusted that very little arsenic volatilizes, and that the copper is just below glowing heat, that is dark in a perfectly dark room, then the domeykite crystals arise from the copper as very thin tabular individuals, often of perfect hexagonal outline. Many of the crystals are only fractional (Fig. 4), and in this case look like bristles or spines, always at right angles to the surface, or if the latter be curved then the bristles will be in radial position. At first a few scattered crystals will come out, always nearest to the supply of arsenic, but later the entire surface will become covered with bristles. Under these conditions large

and full-faced crystals were never obtained. The largest crystals of the tabular habitus 4-5 millim. with prismatic and pyramidal faces well developed, but striated, so that they did not serve for measurements, were grown in a twenty-four-hour experiment. The crystals are fast to the asbestos of the plug P.

*c. Experiment made January 14, 1901.*—A piece of one-fourth inch copper wire two and one-half inches long was wrapped at one end with asbestos cord so as to form a plug which would support the wire within the incubator in a central position, thus giving a chance for free growth in all directions. At the end of fourteen hours the wire had been modified as shown in Fig. 5. The result was unexpected, probably owing to the change of current in the early morning, when the dynamo current had replaced the storage battery and the temperature had risen beyond the intended point.

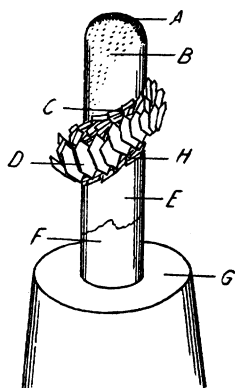


Fig 5

It is, however, all the more instructive, although a failure of the intention. Exceptionally large and fine crystals were expected to form by the arrangement, hence the failure. Instead seven distinct zones appeared, each telling a different story. Zone 1st (*a*). The end of the wire nearest to the asbestos plug and the arsenic and in the centre of the heated field is completely fused, showing a lead-gray color and dull compared to its neighbor. The end is deeply converted into arsenide and this has been fused. Zone 2d (*b*). Bright gray of the color of antimony, a jumble of crystalline faces, but no crystals, has been partly fused. Zone 3d (*c*). A narrow strip of small but well-formed crystals, which belong to



thick tabular type, has not been fused. Zone 4th (*d*). A collar of bristling hexagonal plates, some with prismatic and pyramidal faces, but withal belonging to the thin type. This collar of crystals looks jet-black, the contrast with the bright gray both striking and beautiful. In different light the crystals always appear black, only in reflected light the color is gray. This zone marks the minimum of temperature at which combination of copper and arsenic takes place. Zone 5th (*h*). Is very narrow and dull gray; it reveals miniature crystals of the thin type. Zone 6th (*l*). Shows the beautiful pale red color of pure copper. Evidently arsenic vapors surrounded this part of the wire; the temperature sufficed to let this arsenic combine with the oxygen of the surface, and thus give the latter the pure copper color, the peroxyd subliming. Next to this we find the wire with the usual red color due to a thin film of cuprous oxide.

*d*. A piece of quartz two inches long and just wide enough to go into my largest combustion tube, that is three-fourths inch, had a number of native copper crystals, pseudomorphous after quartz. This specimen was incubated. A growth of thick tabular domey-kite crystals formed all over the one side of the quartz. The artificial nature is disguised by the quartz and the epidote in the association to such an extent that any mineralogist would take it as a thoroughly natural production and hence a most unique specimen.

## 2. ACTION OF ARSENIC VAPORS UPON ALLOYS OF COPPER, NICKEL AND COBALT—MOHAWKITE, KEWEENAWITE.

An alloy was made of the three metals in about the same proportion in which they are found in the natural mohawkite, that is

$$\begin{array}{r} \text{Cu} = 74 \\ \text{Ni} = 21 \\ \text{Co} = 5 \\ \hline 100 \end{array}$$

The alloy was cast into a bar one-fourth inch wide, and parts of this bar were successively exposed in the incubator under different conditions of temperature, of rapid or slow evaporation of arsenic.

*First Experiment, December 18, 1900.*—The alloy is converted into filings and these are put directly against the plug P in the

manner as described under copper, but the filings only occupied the lower half of the tube. Upon the upper flat surface crystals form of the thick tabular type, the first pyramid prevailing over the basal plane. The crystals are coherent laterally, crustlike, over a loose aggregate of bright, light gray crystalline matter with indistinct faces. At the time I thought these two materials were alike. But recently, on re-examination, it is seen that whilst the crystals have become much tarnished, the gray material has not changed at all. The crystal layer was detached as much as possible from the loose substance, for the analysis, but it was not possible to do this thoroughly.

The analysis of the crystals gave (0.216 gram) :

$$\begin{array}{rcl} \text{Cu} = 66.37 : 63 & = & 1.0524 \\ (\text{Ni} + \text{Co}) = 2.43 : 58.6 & = & 0.0415 \\ \text{As} = 30.90 : 75 & = & 0.4120 \\ \hline & & 99.70 \end{array} \left. \vphantom{\begin{array}{l} \text{Cu} \\ (\text{Ni} + \text{Co}) \\ \text{As} \end{array}} \right\} 1.0939$$

Ratio :

$$(\text{CuNi Co}) : \text{As} = 2.655 : 1.000$$

The analysis of the gray loose material gave (0.2325 gram) :

$$\begin{array}{rcl} \text{Cu} = 44.30 & : 63 & = 0.7032 \\ \text{Ni} = 12.54 & \left. \vphantom{\begin{array}{l} \text{Ni} \\ \text{Co} \end{array}} \right\} : 58.6 & = 0.2822 \\ \text{Co} = 4.00 & & 0.9854 \\ \text{As} = 39.25 & : 75 & = 0.5230 \\ \hline & & 100.09 \end{array}$$

Ratio :

$$(\text{CuNi Co}) : \text{As} = 1.88 : 1.00 = 2 : 1$$

This then is typical Keweenawite, described recently by me (*Amer. Journ. Sci.*, Vol. xiv, December, 1902) as found at the Mohawk mine. The non-tarnishing quality is inherent also in the natural mineral, as mentioned *l. c.* The crystals on the other hand are mohawkite; the excess of arsenic making the ratio 2.655 : 1 instead of 3 : 1 is explained by the impossibility of separating the crystals from the adhering keweenawite.

*Experiment of December 24, 1901.*—Instead of filings, two fragments of the alloy were exposed in the incubator for twenty-seven hours. Hexagonal plates, very thin, formed upon a crust of gray material strongly crystalline. The plates stood at right angles to the surface and could be brushed off with small camel's-hair brush.

The analysis with 0.0867 gram of the absolutely pure crystals gave :

$$\begin{array}{rcl}
 \text{Cu} = 69.31 : 63 & = 1.1002 & \} \\
 (\text{Ni} + \text{Co}) = 2.70 : 58.6 & = 0.0461 & \} \quad 1.1463 \\
 \text{As} = 28.12 : 75 & = & \quad 0.3750 \\
 \hline
 & 100.13 &
 \end{array}$$

Ratio :

$$(\text{CuNi Co}) : \text{As} = 3.06 : 1.00 = \text{mohawkite}$$

Both experiments show conclusively that nickel and cobalt will enter the crystals without changing the hexagonal symmetry; that domeykite and mohawkite are indeed isomorphous. At the same time the interesting fact is to be dealt with that nickel and cobalt do not pass into the arsenide with the copper in the ratio in which the alloy exposes them to the action of the arsenic vapors. That in fact the ionic mobility of nickel and cobalt is only approximately one-sixth that of the copper. For in the alloy the ratio of copper to nickel and cobalt is nearly 4 : 1, whilst in the crystals it is 25 : 1. The highest percentage of Ni + Co furnished for mohawkite was 4.51, but the analysis was otherwise unsatisfactory.

### 3. ACTION OF ARSENIC VAPORS UPON NICKEL.

Two cakes of nickel were exposed in the incubator for twenty-four hours. No crystals could be obtained, not even of the most imperfect type. A brittle material formed as a thin crust of a dull gray color. It was not analyzed. The action upon cobalt was similar. The ionic mobility of these metals under these conditions seems to be near zero. We may infer that in the previous experiments Ni and Co were moved by infection from the copper's ionic vigor.

### 4. ACTION OF ARSENIC VAPORS UPON AN ALLOY OF COPPER WITH SILVER—ARGENTODOMEYKITE.

The metals were melted together in the proportion 9 : 1. The alloy was cast into a bar and fragments of this were exposed in the incubator.

*Experiment of January 22, 23, 1901.*—The material for action is a solid piece of the bar about 15 x 25 millimeters. The crystals grew out of this alloy towards the arsenic as rapidly as out of pure copper. They are of the tabular variety, medium thickness. The

pyramidal faces are hollow (see Dr. Wright's Fig. 3). The dark gray crystals are surrounded at the base by a fringe of *silver-white crystals* of the thin plate type. It happened that the exposure began about 9 A.M. on a Saturday morning. At 6 P.M. the crop of crystals had developed finely, but I hoped that they would become extra large by longer exposure. On Sunday I was prevented from going to the laboratory, and on my arrival on Monday I found the incubator barely warm to the touch. The storage battery had run down over Sunday, and to this accident we owe this beautiful and interesting preparation which I now hold in my hand. On seeing the silver-white crystals I thought, first thing, that I was beholding a silver arsenide, but the analysis proved my judgment to have been in error.

The composition is

$$\begin{array}{rcl} \text{Cu} = 80.49 : 63 & = & 1.2773 \\ \text{Ag} = 2.60 : 107.6 & = & 0.0242 \\ \text{As} = 16.93 : 75 & = & 0.2257 \end{array} \left. \vphantom{\begin{array}{l} \text{Cu} \\ \text{Ag} \\ \text{As} \end{array}} \right\} 1.3015$$

Hence the ratio :

$$(\text{CuAg}) : \text{As} = 5.77 : 1 = 6 : 1$$

This substance then is *argentoalgonite*.

The dark gray crystals have the composition :

$$\begin{array}{rcl} \text{Cu} & = & 70.40 \\ \text{Ag} & = & 2.30 \\ \text{(By difference) As} & = & 27.30 \\ \hline & & 100.00 \end{array}$$

This is the ratio :

$$(\text{CuAg}) : \text{As} = 3 : 1$$

or what I will name *argentodomeykite*, which we shall, sooner or later, find undoubtedly as a natural mineral. But how about the algonite? In no other experiment was it observed. Since the form of the crystals is identical with the argentodomeykite, I venture to assert that the algonite is pseudomorphous after the domeykite, and owes its existence to a retrogressive process in this way: when the temperature was slowly going down (with the current from the battery) the arsenical atmosphere became more and more rarefied with the greed of the metallic copper still active. Hence the copper began to draw the arsenic from the nearest

domeykite crystals and the latter became algodonite. Since the algodonite is only found at the base, near the copper, the explanation seems to me plausible enough.

*Experiment of January 5, 6, 1901.*—A piece of silver was exposed in the incubator. It was supposed to be quite pure; but, as will be seen from the analysis, it contained several per cent. of copper. For several hours no action appeared to take place, behavior being similar to nickel. Then the edges began to round and towards evening the piece of alloy went into complete fusion at a temperature certainly not above  $450^{\circ}$  C. Seen by candle-light, through the glass tube, the material had the appearance of a large drop of mercury, being seemingly very mobile. The following morning (with the weaker current) it was found solidified, but no sign of crystals. The substance broke readily under the hammer; the fracture shows cleavage faces and a light gray color.

The analysis gave (0.4795 gram):

		<i>Atoms.</i>	
Ag =	74.32	0.688	} 0.763
Cu =	4.72	0.075	
(Difference) As =	20.96		0.273
	<hr/>		
	100.00		

Ratio:

$$(\text{AgCu}) : \text{As} = 2.79 : 1.00$$

There is, therefore, a molecule  $\text{Ag}_3\text{As}$  with a tendency, however, to pass into  $\text{Ag}_2\text{As}$ ; some of the latter is shown in the ratio  $\frac{2}{3}$ , instead of 3, which corresponds exactly to  $4 \text{ Ag}_3\text{As} + \text{Ag}_2\text{As}$ .

*Experiment of January 21, 1901.*—Piece of alloy (1 copper, 1 silver) exposed twenty-one hours. A beautiful growth of thick tabular crystals, which sit up on a gray crystalline layer, under which appears a thin zone, silver-white in color,  $\frac{1}{2}$  millimeters thick; then comes copper-red. The growth is entirely in the axis of the piece and tube towards the arsenic.

The analysis of the crystals gave:

Cu =	62.02	0.9844	} 1.0882
Ag =	11.21	0.1038	
As =	26.77		0.3569
	<hr/>		
	100.00		

Ratio:

$$(\text{CuAg}) : \text{As} = 3.05 : 1.00$$

The silver-white zone under the crystals demonstrates to the eye the difference in the ionic mobility of copper and silver. One sees how the copper is drawn away from the silver. It would be of interest to know whether the outermost crystals carry less silver than those nearest the metallic base, but as this gain of knowledge would also involve a destruction of the specimen I abstained, satisfied with the average result as exhibited in the above analysis.

*Experiment of February 24, 1901.*—An alloy of 1 copper with 1 silver was made and a piece weighing about 5 grams was exposed in the incubator for fourteen hours (over night). The front and upper surface of the ingot was found covered with crystals. They are not good, but they show distinctly the habitus of the thick tabular domeykite. There is no tendency to rise; the silver is evidently as little mobile as the nickel and acts depressingly upon the activity of the copper. The crystals are laterally grown together, forming a strongly cohering crust, which cracks off with the hammer blow.

Analysis of the crust gave (0.3057 gram):

		<i>Atoms.</i>	
	Cu =	55.87 = 0.887	} 1.026
	Ag =	15.01 = 0.139	
(By difference)	As =	29.12 =	
		<hr/>	0.388
		100.00	

Ratio:

$$(\text{CuAg}) : \text{As} = 2.65 : 1.00$$

This corresponds to a mixture of 5 (CuAg)<sub>2</sub>As with 3 (CuAg)<sub>2</sub>As. The tendency is always rather for the building up of Cu<sub>3</sub>As than of Cu<sub>2</sub>.

*Experiment of February 28, 1901.*—A piece of alloy 1 Cu + 1 Ag exposed in incubator for two days and nights at very low temperature. The end reaching towards the arsenic showed a fused, bluish-gray, apparently homogeneous material. At the opposite end are small crystals with bright faces. Habitus: steep hexagonal pyramid with striated sides, capped by the normal or fundamental pyramid.

Analysis with 0.3412 gram gave:

		<i>Atoms.</i>	
	Cu =	40.94 = 0.650	} 0.989
	4 Ag =	36.62 = 0.339	
(By difference)	As =	22.44 =	
		<hr/>	0.2992
		100.00	

Ratio:

$$(\text{CuAg}) : \text{As} = 3.3 : 1.00$$

This is the single instance in which the metal exceeds the  $\frac{3}{1}$  ratio, if we exclude the instance of the algonite. I venture to explain it by a similar process of retrogression, or, perhaps, better, by ingression of the still very mobile metal ions into the molecule  $\frac{3}{1}$  after the arsenic vapor had become too rarefied for addition from the outside, as the temperature was sinking—*i.e.*, the current going down. All the experiments with the copper-silver alloy prove:

1. Silver and copper together replace one another isomorphously in the molecule  $\frac{3}{1}$ .
2. The representation is 63 Cu by 107.6 Ag—*i.e.*, divalent copper with monovalent silver.
3. There is a molecule,  $\text{Ag}_3\text{As}$ , whose melting-point is below the temperature of formation; hence not crystallizable in the incubator.
4. Higher temperature tends to forming  $\text{Ag}_3\text{As}$ , same as  $\text{Cu}_3\text{As}$ .

#### 5. THE ACTION OF ARSENIC VAPORS UPON AN ALLOY OF COPPER AND ANTIMONY—STIBIHOMEYKITE.

If copper and antimony were melted together in such proportion as  $\text{Cu}_3\text{Sb}$ , which corresponds nearly to copper 3 parts, antimony 1 part, in percentage  $\text{Cu} = 75.6$ ,  $\text{Sb} = 24.4$ , and such an alloy were to be exposed at the proper temperature to the arsenic vapors, one might be justified in supposing that by simple addition of one atom of As we would get



if there were a tendency in the elements to form such a combination; or if the molecule  $\text{Cu}_3\text{Sb}$  ( $\text{Cu} = 66$   $\text{Sb} = 34$ ) were exposed, then one As might couple together two molecules of  $\text{Cu}_3\text{Sb}$ .

*Experiment of February 1, 2, 3, 1901.*—The alloy  $\text{Cu}_3\text{Sb}$  was exposed for three days and nights at very low temperature. In the absolutely dark room the wire coil showed dull redness. Very large tabular crystals form, drawn in the axis of the tube forward the arsenic. The crystals have the color and habitus of domey-kite. Their composition is:

	Cu =	69.34
(0.1422 gram)	Sb =	1.26
(By difference)	As =	29.40
		<hr/> 100.00

Ratio:

$$\text{Cu} : (\text{AsSb}) = 2.76 : 1.00$$

The analysis reveals two points: 1. Arsenic does not add itself to a ready-formed molecule  $\text{Cu}_3\text{Sb}$ . The same preferential attraction towards copper comes into play as in the case of the metallic constituents of copper alloys. The ionic mobility of antimony is low; at any rate, at the low temperature in use during this experiment. 2. The ratio indicates that antimony is probably merely mechanically carried along so long as copper is at hand for the arsenic; for if antimony be considered out of the molecule the ratio will be  $\text{Cu} : \text{As} = 2.82 : 1.00$ . But even this is unsatisfactory for a crystallized body with no mechanical admixture likely, for the crystals were all separate and large enough to be fully scrutinized.

For more light I went to examine into the material directly under and back of the large crystals. This material is loose, in small loose grains of angular habitus, not scaly at all, as the large crystals. Habitus quite unlike that of the domeykite; color darker gray. The analysis of this material (0.0570 gram) gives:

$\text{CuO} = 0.0393$	$\text{Cu} = 55.44$	:	63 =	0.08800
$\text{Sb}_2\text{S}_3 = 0.0028$	$\text{Sb} = 3.51$	:	122 = 0.0287	} 0.571
$\text{As}_2\text{S}_5 = 0.0480$	$\text{As} = 40.66$	:	75 = 0.5421	
<hr/>				99.61

Ratio:

$$\text{Cu} : (\text{AsSb}) = 880 : 571 = 3.08 : 2$$

As the copper becomes scarce, the arsenic being still plentiful, this new  $3/2$  molecule forms. In spite of the superabundance of antimony, the selection of copper continues. With nickel we saw in similar conditions the forming of  $2/1$  molecule. The affinity for antimony is quite low, and yet it is probably the influence of the latter through which  $3/2$  and not  $2/1$  are brought into being. The excess of arsenic in the large crystals accounts for itself by the presence of this  $3/2$  molecule under the influence of antimony.

*Experiment of February 4, 1901.*—The same alloy  $\text{Cu}_3\text{Sb}$  was exposed for thirty-six hours at a higher temperature, about  $550^\circ \text{C}$ . Two products were obtained. Forward, towards the arsenic, a lustrous gray mass, apparently of fused crystals. The outermost part of this mass was broken off, revealing a hollow center, an inner layer of dark-gray mass, an outer layer of lighter color. Could not separate the two. Let this be material ( $\alpha'$ ). The second substance



is composed of crystals of the domeykite habitus, thin and thick tabular; all but very few show rounded edges—that is, incipient fusion. A part of the crystals was removed. Material (*a*).

Analysis of *a* (0.4801 gram); many individual plates, others grown together.

$$\begin{array}{rcl} \text{Cu} = 69.79 : 63 = & & 0.1078 \\ \text{As} = 20.32 : 75 = 0.2709 & \} & \\ \text{Sb} = 9.74 : 122 = 0.0800 & \} & 0.3509 \\ \hline & & 99.85 \end{array}$$

Ratio :

$$\text{Cu} : (\text{AsSb}) = 3.11 : 1.00$$

These crystals are thus proved to be *stibiodymeykite*. It also follows that higher temperature increases the ionic mobility of the antimony.

The analysis of the material (*a'*) (0.4823 gram) gives :

$$\begin{array}{rcl} \text{Cu} = 45.10 : 63 = & & 0.7158 \\ \text{Sb} = 36.83 : 122 = 0.3019 & \} & \\ \text{As} = 18.07 : 75 = 0.2409 & \} & 0.5428 \\ \hline & & 100.00 \end{array}$$

Ratio :

$$\text{Cu} : (\text{SbAs}) = 1.32 : 1.00 = 4 : 3$$

I take this to mean a mixture in which the outer crust is  $\text{Cu}(\text{SbAs})$ , whilst the inner layer is  $\text{Cu}_3(\text{SbAs})_2$ ;  $1/1 + 3/2 = 4/3$ .

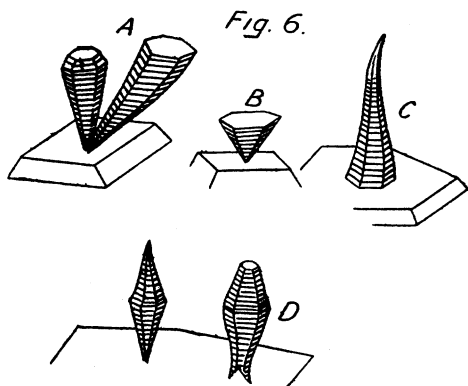
*Experiment of February 7.*—A fragment of the alloy  $\text{Cu}_3\text{Sb}$  was again exposed with the intention of keeping the temperature, if possible, below that of the one preceding, and yet higher than in the first experiment. The exposure was forty hours. It must be remembered that owing to the local conditions a perfectly uniform temperature could not be maintained unless the ammeter were under steady observation—an impossible or at any rate too difficult a proposition. Hence the temperature would steadily decrease, whilst the potential sank from 120 to 110 volts and would rise (during the night) to 125 volts, when in the forenoon the dynamo was coupled to the storage battery.

The original alloy was found covered with three products :

1. A fine granular crust.
2. Over this a peculiar sort of crystals not showing any one of

the habitus of domeykite. These crystals are all fused together laterally; the faces are rough like the leaves of reeds. They are not measurable.

3. On these faces rise curious pyramidal forms as shown in Fig. 6. The crystals are slender and small. Their faces are bent and very uneven from the alternation of pyramid and prism. The acute pyramid predominates, but apex is closed by the normal pyramid



(see Dr. Wright). Some of the forms, as at *a.a.*, resemble minute cup corals; others, as at *b.d.*, imitate a club, whilst *c.c.* may be likened to a church steeple.

*ad.* 1 and 2. Crust and crystals cannot be separated.

Analysis gives (0.0532 gram):

$$\begin{array}{rcl}
 \text{Cu} & = & 67.74 : 63 = 1.0752 \\
 \text{Sb} & = & 1.00 : 122 = 0.0082 \\
 \text{(Difference) As} & = & 31.26 : 75 = 0.4168 \\
 \hline
 & & 100.00
 \end{array}$$

Hence ratio:

$$\text{Cu} : (\text{AsSb}) = 2.52 : 1 = 5 : 2$$

Corresponding to a molecular mixture:

$$3'/1 + 2/1 = 5'/2$$

*ad.* 3. The crystals are so small that the whole of them would not make 0.1 gram. The sacrifice of any of them came hard. 3.97 milligrams weighed on a button balance, which is accurate to

0.005 mg., was dissolved in  $\text{HNO}_3$  and evaporated to dryness. The dry mass dissolves in water, to which a drop of dilute  $\text{H}_2\text{SO}_4$  has been added. Solution is without opalescence. Hence *antimony* can only be present in traces. Then 2.78 mg. of fine copper wire was dissolved in  $\text{HNO}_3$ , this being just seventy per cent. of the arsenide. Both solutions made ammoniacal were compared in proper dilution of 50 cc. on the colorimeter. The color of the solution from the pure copper is slightly lighter and by adjustment brings the percentage

$$\text{Cu} = 72$$

The crystals are thus proven to be *domeykite* and not stibiodomeykite. The strange habitus of the crystals, so unlike that of the prevalent habitus, must be looked for in the influence of the antimony, though the latter does not itself enter the composition.

#### 6. ACTION OF ARSENIC VAPORS UPON ZINC.

*Experiment of March 2, 1901.*—A piece of chemically pure zinc, broken from a stick, was exposed for twenty hours. The surface is covered by a crust which is developed into mamillary groups, somewhat like psilomelane. The crust detaches itself by a blow from the hammer and breaks into flaky pieces resembling graphite.

Analysis gives (0.222 gram):

$$\text{ZnO} = 0.1720 = 0.1381 \text{ Zn}$$

Hence

$$\begin{array}{r} \text{Zn} = 62.20 \\ \text{(By difference) As} = 37.80 \\ \hline 100.00 \end{array}$$

$$\text{Zn} : \text{As} = 959 : 504 = 1.902 : 1$$



Zinc acts toward arsenic vapors like nickel; the ratio 2/1 seems to be the normal.

#### 7. ACTION OF ARSENIC VAPORS UPON LEAD.

The lead melts. Exposure for twenty hours. Product is still

malleable to some extent, but breaks off short when nicked with the chisel and then bent. Looks homogeneous.

Analysis gave :

$$\begin{array}{r} \text{Pb} = 96.10 \\ \text{As} = 3.75 \\ \hline 99.85 \end{array}$$

$$\text{Pb} : \text{As} = 0.4637 : 0.050 = 9.27 : 1$$

The ratio is that of whitneyite. The ionic mobility is small.

MICHIGAN COLLEGE OF MINES, May, 1903.

## CRYSTALLOGRAPHIC PROPERTIES.

BY FRED EUGENE WRIGHT.

The following group of artificial minerals, which Dr. Koenig has kindly intrusted to me for crystallographic investigation, is characterized by high metallic luster, tin-white to steel-gray and even black color, conchoidal fracture and hardness : 3-4. The crystals obtained are all small and rarely exceed a millimeter in length. The character and quality of the crystal faces is not uniform for the whole group. Those of domeykite are usually sharp, well formed and furnished single reflection signals on the goniometer, whereby a fairly exact determination of its elements could be obtained. The crystals of the remaining minerals are far less perfect, their uneven undulating faces evincing such indistinct, manifold reflexion signals on the goniometer that an accurate determination of their elements was impossible.

The crystals were measured on a Goldschmidt's two-circled goniometer (model 1901), with attachment for observing small, weak faces and an electric arc goniometer lamp.<sup>1</sup>

<sup>1</sup> The electric goniometer lamp (Fig. A) consists of a box (*a*) made of Russian sheet iron, lined with asbestos cardboard, and of an electric lamp (*b*). The back of the box (*a*) is left open to allow the insertion of the electric lamp—a small black movable curtain serving to shut off all false light, which might disturb in measuring. The mirror (*d*) and cap (*e*) are used to light the verniers and were taken bodily from a Goldschmidt's Auer burner gas goniometer lamp (see *Zeitschrift für Krystallographie*, Bd. xxiii, 1894, p. 149. V. Goldschmidt. Eine neue Goniometer-lampe). The electric lamp (*b*) is the No. 10, hand feed, of J. B. Colt & Co., Chicago, Ill. (price, \$10), together with an adjustable rheostat (seven to eighteen ampères, \$13). By means of the latter the intensity